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A THIOCARBOXYLATE COMPOUND
AND A PRODUCTION METHOD THEREOF

[Chiokarubonsan esteru kagohbutsu oyobi sono seizoh houhoh]

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[The Requested Amendments have been incorporated into the text of this translation]

[In this translation, product names are spelled phonetically.]

Specification

1. Title of the invention

A thiocarboxylate compound and manufacturing method thereof

2. Claim of the invention

(1) The thiocarboxylate compound shown in the following general formula



[Wherein, R^1 is a hydrogen atom or methyl group, R^2 and R^3 are the same or different and are hydrogen atoms or alkyl groups, R^4 is a substituted or nonsubstituted alkyl groups, substituted or nonsubstituted aralkyl groups, or substituted or nonsubstituted aryl group, and m is an integer in the range of 2 or higher.]

(2) A production method for the thiocarboxylate compound described in Claim (1) of the invention consisting of a reaction of a compound represented by the following general formula



[Wherein, R^2 and R^3 are the same or different and are hydrogen atoms or alkyl groups, R^4 is a substituted or nonsubstituted alkyl group, substituted or nonsubstituted aralkyl group, or substituted or nonsubstituted aryl group, and m is an integer in the range of 2 or higher.] and a compound represented by the following general formula



[Wherein, R^1 is a hydrogen atom or methyl group, and R^5 is an hydroxyl group, chlorine atom, or an alkoxy group.].

3. Detailed description of the invention

[Field of industrial application]

The present invention pertains to a polymeric thiocarboxylate compound suitable for optical materials and can be used effectively for paints, inks, adhesives, photosensitive resins, etc., and a manufacturing method thereof.

[p. 2]

[Prior art]

Many studies have been conducted on synthetic resins used in the place of inorganic glasses in recent years, but the refractive index of synthetic resins, for example, diethylene glycol bisallyl carbonate, is low, approximately 1.50, in comparison to that of inorganic glass.

A variety of resins with high refractive indexes without the above-mentioned problem have been proposed. For example, resins with a high refractive index such as polycarbonate and polysulfone, etc. have been proposed. The refractive index of the above-mentioned resins is high, approximately 1.60, but problems such as low light transmittance, poor optical uniformity, and discoloration pose problems.

Thus, crosslinkable monomers for resins with a high refractive index having an aromatic ring in the structure are proposed in Japanese Kokai [Unexamined] Patent Application No. Sho 61[1986]-28901, Japanese Kokai [Unexamined] Patent Application No. Sho 60[1985]-197711, etc. An increase in the refractive index can be achieved in resins with a high refractive index produced upon polymerization of the above-mentioned monomers, but the volume of the aromatic ring included in the molecule is high in the raw material monomer, thus, the resin is

hard but brittle, which are characteristic of the aromatic ring, and impact resistance is poor.

Meanwhile, as a means to increase the impact resistance, a method whereby a copolymerization reaction is carried out with a monomer having a molecular chain structure comprising a high volume of oxyalkylene group in the molecule such as polyethylene glycol (meth)acrylates is known. Furthermore, a resin with a high refractive index having a polymeric monomer containing an alkylene group as the main component is proposed in Japanese Kokai [Unexamined] Patent Application No. Hei 1[1989]-115910.

However, in each of the above-mentioned monomers, the longer the molecular chain structure of the alkylene group or oxyalkylene group, the greater the impact resistance of the resulting polymer; however, a reduction in the refractive index takes place, as well.

Thus, it is not possible to produce a resin with a high refractive index having high impact resistance.

[Problems to be solved by the invention]

The objective of the present invention is to produce a monomer capable of producing a resin with a high refractive index having high transparency, high weather resistance, and high impact resistance.

[Means to solve the problem]

As a result of much research conducted by the present inventors in an effort to eliminate the above-mentioned existing problems, they discovered that a thiocarboxylate compound having a specific structure is the answer and the present invention was accomplished.

In other words, the present invention is a thiocarboxylate compound represented by the following general formula [I]



[Wherein, R^1 is a hydrogen atom or methyl group, R^2 and R^3 are the same or different and are hydrogen atoms or alkyl groups, R^4 is a substituted or nonsubstituted alkyl groups, substituted or nonsubstituted aralkyl groups, or substituted or nonsubstituted aryl group, and m is an integer in the range of 2 or higher.]

In the above-mentioned general formula [I], R^2 and R^3 can be the same or different and are hydrogen atoms or alkyl groups, and from the standpoint of application of the polymer produced by the polymerization reaction as an optical material, it is especially desirable when the above-mentioned groups are either hydrogen atoms or methyl groups.

In the above-mentioned general formula [I], R^4 is a substituted or nonsubstituted alkyl group, substituted or nonsubstituted aralkyl group, or substituted or nonsubstituted aryl group. The number of carbon atoms of the above-mentioned alkyl group is not especially limited, but from the standpoint of the refractive index of the polymer produced by the polymerization reaction, 1~5 carbon atoms is especially desirable. And for example, a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, sec-butyl group, tert-butyl group, n-pentyl group, etc. can be mentioned. The number of carbon atoms of the above-mentioned aralkyl group is not especially limited, but from the standpoint of the refractive index of the polymer produced by the polymerization reaction, 7~10 carbon atoms is especially desirable. For example, a benzyl group, phenyl ethyl group, phenyl propyl group, etc. can be mentioned.

Furthermore, for the above-mentioned aryl group, the number of carbon atoms is not especially limited, and for the reasons given above, 6~10 carbon atoms is desirable. For example, a phenyl group, tolyl group, xylyl group, naphthyl group, etc. can be mentioned.

[p. 3]

Substituents for the above-mentioned alkyl group, aralkyl group, or aryl group represented by R^4 above are not especially limited, and a halogen atom, alkoxy group, alkyl thio group, phenyl group, phenyl thio group, etc. can be mentioned. As typical examples of substituted alkyl groups, substituted aralkyl groups, and substituted aryl groups, halogenoalkyl groups such as a chloromethyl group, bromomethyl group, or trichloromethyl group, halogenoaralkyl groups such as chlorobenzyl group, bromobenzyl group, chlorophenylethyl group, bromophenylethyl group, and dichlorobenzyl group, halogenoaryl groups such as chlorophenyl group, bromophenyl group, dichlorophenyl group, and dibromophenyl group, methylthiobenzyl group, methylthiophenyl group, di(methylthio)benzyl group, phenylthiobenzyl group, phenylthiophenyl group, biphenyl group, etc. can be mentioned.

Furthermore, m is an integer in the range of 2 or higher in general formula [I] above. In general, the higher the value of the m , the higher the sulfur content per molecule; thus, an increase in refractive index as well impact resistance of the resin produced upon polymerization is observed. However, when the value of m is too high, heat-resistance of the resin produced is reduced. Therefore, it is desirable for the value of the m to be in a range of 2~6, preferably, 2~4 from the standpoint of the refractive index, impact resistance, and heat-resistance of the resin produced.

In order to achieve a high refractive index and low dispersibility of the polymer produced upon performing a polymerization reaction for the thiocarboxylate compound of the present invention, it is desirable when R^4 in the above general formula [I] to be a substituted or nonsubstituted aralkyl group.

The thiocarboxylate compound represented by the above-mentioned general formula [I] of the present invention can be identified and confirmed using the method described below.

(a) Upon measurement of the infrared absorption spectra (IR), an absorption based on the CH bond at 3150~2800 cm^{-1} , an absorption based on the end double bond at 1650-1620 cm^{-1} ; furthermore, the intense absorption of carbonyl group at around 1660~1690 cm^{-1} based on the thioester bond is observed.

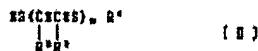
(b) Identification of the compound can be easily achieved upon measurement of the ^1H -nuclear magnetic resonance spectra ($^1\text{H-NMR}$). Especially, in the case when R^1 is a methyl group in general formula [I], the peak based on the methyl group unique to methacrylate is observed at around δ 1.9 ppm, and peaks based on the vinylidene proton are observed at around δ 5.7 and δ 6.1 ppm at a ratio of 3:1:1. Furthermore, in the case when R^1 is a hydrogen atom, three peak region of hydrogens unique to acrylate are observed at δ 5.6~7 ppm. Furthermore, in the case of a thioether chain, the peak of the pattern according to each bonding state of the hydrogen on the carbon atom bonded with the sulfur atom is shown at around δ 2.9 ppm. Furthermore, when one or the other of R^2 and R^3 is a methyl group, a doublet is recognized at around δ 1.1 ppm. Furthermore, in the case when R^4 is an aralkyl group, the peak based on hydrogen on the carbon atom bonded with a phenyl group is recognized. For example, in the case of benzyl group, singlet is recognized at around δ 3.7 ppm, and the peak having a pattern

according to each bonding state is recognized at around δ 2.6 ppm. Furthermore, in the case when an aromatic hydrogen exists, the peak is recognized at around δ 7 ~ δ 8.5 ppm, and when an aliphatic hydrogen exists, the peak is observed at around δ 1 ~ δ 2 ppm. In addition, when a hydrogen atom exists, a spectral pattern based on the bonding mode is shown. Identification of the compound can be easily achieved based on the above information.

(c) The percentage by weight of oxygen can be calculated when the percentage by weight of carbon, hydrogen, and sulfur is obtained by means of elemental analysis and the sum of the percentages by weight of each element recognized is deducted from 100, and the compositional formula of the compound can be determined.

The thiocarboxylate compound represented by general formula [I] can be produced using any method, but, in general, the method explained below is used.

Namely, a method wherein a reaction is conducted for a compound represented by the following general formula [II]



[Wherein, R^2 and R^3 are the same or different and are hydrogen atoms or alkyl groups, R^4 is a substituted or nonsubstituted alkyl group, substituted or nonsubstituted aralkyl group, or substituted or nonsubstituted aryl group, and m is an integer in the range of 2 or higher.]

[p. 4]

and a compound represented by the following general formula [III]



[Wherein, R¹ is a hydrogen atom or methyl group and R⁵ is a hydroxyl group, chlorine atom, or alkoxy group.]

(a) Method wherein a carboxylic acid is used

It is possible to produce the thiocarboxylate compound represented by general formula [I] when a dehydration condensation reaction is carried out for the compound represented by general formula [II] and a carboxylic acid where R⁵ is a hydroxyl group in the compound represented by general formula [III] in the presence of an acid catalyst. The charged molar ratio of the two raw materials is determined accordingly, and in general, an excess amount of one or the other compounds is used. For the acid used as a catalyst in the above-mentioned reaction, mineral acids such as hydrochloric acid and sulfuric acid, aromatic sulfonic acids and Lewis acids such as fluoroboroethylate can be mentioned.

Formation of water as a byproduct occurs in the above reaction, but the reaction is an equilibrium reaction; thus, refluxing is carried out for the solvent with Dean-Stark moisture separator or by pouring a dehydrating agents such as anhydrous sodium sulfate and a molecular sieve into a Soxhlet extractor, or adding a dehydrating agent such as N,N-dicyclohexylbarbodiimide to the reaction system so as to remove water from the system. For the solvent used in this case, an aromatic hydrocarbon such as benzene or toluene, an aliphatic hydrocarbon halide such as chloroform or dichloromethane can be mentioned.

The reaction temperature varies depending on the type of the solvent used, but, in general, a temperature in the range of 0EC and 120EC is desirable. The reaction time varies depending on the type of raw material used, but, in general, 30 minutes to 20 hours is suitable, and 1 hr to 6 hours is even more desirable. The method used for isolation and purification of the

target material, namely, the compound represented by general formula [I] above, from the reaction system is not especially limited, and known methods can be used in this case as well.

(b) Method wherein a carboxylic acid chloride is used

It is possible to produce the thiocarboxylate compound represented by general formula [I] when a dehydrochlorination treatment is carried out for a compound represented by general formula [II] and a carboxylic acid chloride where R^5 is a chlorine atom in the compound represented by general formula [III] in the presence of a base. In general, the charged molar ratio of the two raw materials is selected to be in the range of (compound represented by general formula [II])/(compound represented by general formula [III]) = 0.8~1.5, and it is desirable when an equivalence is used.

Hydrogen chloride is produced as a byproduct in the above reaction. In general, it is desirable when a base is included in the reaction system as a hydrogen chloride scavenger or an inert gas such as nitrogen gas is supplied to the reaction system to remove the hydrogen chloride from the reaction system.

The base used for the above-mentioned hydrogen chloride scavenger is not especially limited, and known bases can be used. For bases commonly used, trialkylamines such as trimethylamine, triethylamine, and tripropylamine, pyridine, tetramethylurea, sodium hydroxide, sodium carbonate, etc. can be mentioned. It is desirable when at least 1 mole of base is used for 1 mole of carboxylic acid chloride.

In general, it is desirable when an organic solvent is used for the above-mentioned reaction. For examples of solvents used effectively in this case, aliphatic or aromatic hydrocarbons, and hydrocarbon halides such as benzene, toluene, xylene, hexane, heptane,

petroleum ether, chloroform, methylene chloride, and ethylene chloride, ethers such as diethyl ether, dioxane, and tetrahydrofuran, N,N-dialkyl amides such as N,N-dimethylformamide, and N,N-diethylformamide, etc. can be mentioned.

The temperature used for the above-mentioned reaction can be selected from a wide range, and in general, a temperature in a range of -20EC to 100EC, preferably 0EC to 50EC can be used effectively. The reaction time varies depending on the type of raw material used, and in general, 5 minutes to 24 hours is adequate, and 10 minutes to 4 hours is especially desirable. It is especially desirable when stirring is provided during the course of the reaction.

The method used for separation and purification of the target material, that is, the compound represented by general formula [I] above, from the reaction system is not especially limited, and known methods can be used in this case as well.

[p. 5]

(c) Method where carboxylate is used

It is possible to produce the thiocarboxylate compound represented by general formula [I] when a transesterification reaction is carried out for the compound represented by general formula [II] and a carboxylate where R⁵ in the compound represented by general formula [III] is an alkoxy group. It is desirable when an acid or a base is used as a catalyst in the above-mentioned reaction. For examples of acids that can be used effectively as a catalyst, sulfuric acid, hydrochloric acid, p-toluene sulfonate, etc. can be mentioned, and for bases, inorganic bases such as sodium hydroxide, potassium hydroxide, sodium carbonate, and sodium hydrogen carbonate, alkoxides such as sodium methoxide and potassium-t-buthoxide, etc. can be mentioned.

An alcohol (R^5H) is produced in the above reaction. The above-mentioned reaction is an equilibrium reaction; thus, it is desirable to remove the alcohol produced from the reaction system by means of standard distillation or azeotropic distillation. Thus, it is desirable when a material with an R^5 comprising an alkoxy group having 1~5 carbon atoms, preferably 1~3 carbon atoms, is used as the raw material carboxylate represented by general formula [III].

In general, the above-mentioned reaction is performed without a solvent, and when the raw material is a solid material, it is desirable when a solvent having a higher boiling point than that of the byproduct alcohol is used.

For examples of solvents used effectively in this case, aromatic hydrocarbons, and halogen substituted aromatic hydrocarbon halides such as benzene, toluene, xylene, chlorobenzene, and dichlorobenzene, N,N -dialkylamides such as N,N -dimethyl formamide, and N,N -diethylformamide, dimethylsulfoxide, etc. can be mentioned.

The temperature used for the above-mentioned reaction varies depending on the type of byproduct alcohol, and in general, a temperature where the byproduct alcohol undergoes distillation is desirable. The reaction time varies depending on the type of raw material used, and in general, 30 minutes to 24 hours is adequate, and 2 hours to 8 hours is even more desirable. It is especially desirable when stirring is provided during the reaction.

The method used for separation and purification of the target material, namely, the compound represented by the above-mentioned general formula [I], from the reaction system is not especially limited, and known methods can be used in this case as well.

The refractive index of the thiocarboxylate compound represented by general formula [I] above of the present invention is high and a polymer having high transparency, weather

resistance, and impact resistance can be produced. It is possible to conduct the polymerization reaction for the above-mentioned compound by itself, but it is desirable when a copolymerization reaction is carried out with other copolymerizable monomers. It is desirable to use the thiocarboxylate compound of the present invention so as to improve the impact resistance without reducing the refractive index through copolymerization with a monomer having an aromatic ring having a high refractive index but low impact resistance. Specific examples of the above-mentioned copolymerizable monomers are listed below. In this case, acrylate and methacrylate are referred to in a generic term of (meth)acrylate.

For monofunctional monomers, styrene, styrene derivatives such as vinyl toluene and methoxy styrene, halogen substituted styrenes such as chlorostyrene, bromostyrene, iodostyrene, dichlorostyrene, dibromostyrene, trichlorostyrene, and tribromostyrene, (meth)acrylates such as methyl (meth)acrylate, phenyl (meth)acrylate, chlorophenyl (meth)acrylate, bromophenyl (meth)acrylate, dichlorophenyl (meth)acrylate, dibromophenyl (meth)acrylate, methoxy phenyl (meth)acrylate, benzyl (meth)acrylate, chlorobenzyl (meth)acrylate, bromobenzyl (meth)acrylate, dichlorobenzyl (meth)acrylate, dibromobenzyl (meth)acrylate, trichlorobenzyl (meth)acrylate, tribromobenzyl (meth)acrylate, pentachlorobenzyl (meth)acrylate, pentabromobenzyl (meth)acrylate, phenoxy ethyl (meth)acrylate, α -naphthyl (meth)acrylate, and β -naphthyl (meth)acrylate, vinyl naphthalenes such as 1-vinyl naphthalene and 2-vinyl naphthalene, 4-vinyl biphenyl and vinyl phenyl sulfide, etc. can be mentioned.

[p. 6]

For the bifunctional monomers, di(meth)acrylates such as ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, 1,4-di(meth)acryloyloxy benzene, 1,3-

di(meth)acryloyloxy benzene, di[(meth)acryloyloxy-phenyl] methane, terephthalic acid-di[2-(meth)acryloyloxy-ethyl], 1,5-di(meth)acryloyloxy-naphthalene, 2,2-bis[4-(meth)acryloyloxy-phenyl] propane, 2,2-bis[4-(meth)acryloyloxy-ethoxy phenyl] propane, 1,4-di(meth)acryloyloxy-2,3,5,6-tetrabrom benzene, di(meth)acryloyloxy-di(4-chlorophenyl) methane, tetrabrom phthalic acid-di[2-(meth)acryloyloxy ethyl], 2,2-bis[4-(meth)acryloyloxy-3-chloro phenyl] propane, 2,2-bis[4-(meth)acryloyloxy-ethoxy-3,5-dibrom phenyl] propane, 2,2-bis[4-(meth)acryloyloxy-3-brom phenyl] propane, 2,2-bis[4-(meth)acryloyloxy-3,5-dibrom phenyl] propane, 1,5-di(meth)acryloyloxy-2,4,6,8-tetrachloro naphthalene, and 1,5-di(meth)acryloyloxy ethoxy-2,4,6,8-tetrabrom naphthalene, allyl compounds such as diallylphthalate, diallyltetraphthalate, and diallylisophthalate, divinyl compounds such as divinyl benzene, etc. can be mentioned. One, or a mixture of two or more different types of the above-mentioned monomers in combination, can be used

The mixing ratio of the above-mentioned copolymerizable monomers and the thiocarboxylate compound represented by general formula [I] can be selected over a wide range. In general, it is desirable when the mixing ratio is selected in such a manner that properties of the copolymerizable monomers are not significantly reduced; thus, it is desirable when 0.5~25 % by weight of the thiocarboxylate compound of the present invention is added for the total monomer composition, and in the range of 1~20 % by weight is further desirable.

It should be noted that a resin with a high refractive index produced by performing a homopolymerization for the thiocarboxylate compound of the present invention or copolymerization with a monomer having one polymeric group among the above-mentioned copolymerizable monomers is a thermoplastic resin. Thus, when the resin is used for

applications where a special treatment is required, it is desirable when a copolymerization reaction is carried out with a monomer having at least two polymeric groups as a copolymerizable monomer.

The polymerization reaction method used for production of a polymer from a monomer composition containing the thiocarboxylate compound represented by general formula [I] of the present invention and other copolymerizable monomers is not especially limited, and standard radical polymerization can be used. As for the means used for initiation of the polymerization reaction, use of a radical polymerization initiator such as a peroxide or an azo compound, application of ultraviolet, α -rays, β -rays, γ -rays, or combinations of the above-mentioned methods may be mentioned. As an example of a typical polymerization reaction method, an injection polymerization reaction method wherein the above-mentioned monomer or monomer composition containing a radical polymerization initiator is injected into the space between molds retained by an elastomer gasket or spacer, curing is performed in an air furnace, and the cured resin is subsequently removed can be mentioned.

The type of radical polymerization initiator used is not especially limited, and standard materials can be used, and as typical examples, diacyl peroxides such as benzoyl peroxide, p-chlorobenzoyl peroxide, decanoyl peroxide, lauroyl peroxide, and acetyl peroxide, peroxy esters such as t-butyl-peroxy-2-ethyl hexanate, t-butyl-peroxy neodecanoate, cumyl peroxyneodecanoate, and t-butylperoxybenzoate, percarbonates such as diisopropyl peroxydicarbonate, di-2-ethylhexylperoxydicarbonate and di-sec-butylperoxydicarbonate, azo compounds such as azo-bis-isobutylonitrile can be mentioned. The mixing ratio of the above-mentioned radical polymerization initiator varies depending on the polymerization reaction

conditions used, type of initiators used, and the composition of the above-mentioned monomers used, and in general, an amount in the range of 0.01~10 parts by weight for 100 parts by weight of the total amount of monomer is adequate, and in the range of 0.01~5 parts by weight is especially desirable.

[p. 7]

Among polymerization reaction conditions, temperature has a significant influence on the properties of the resin with a high refractive index that is produced. The above-mentioned temperature condition is influenced by the type and amount of initiator and the type of monomer used, and in general, it is desirable when a two-stage polymerization reaction wherein the polymerization reaction is started at a relatively low temperature and the temperature is slowly increased and curing is done at a high temperature after the polymerization reaction is completed. Furthermore, polymerization reaction time varies depending on a variety of factors as in the case of the polymerization reaction time, and an ideal time is determined according to the above-mentioned conditions, and in general, it is desirable when the polymerization reaction is completed within 2 to 40 hours.

Needless to say, a variety of additives, for example, release agents, ultraviolet absorbers, antioxidants, coloring inhibitors, antistatic agents, fluorescent dyes, dyes, pigments stabilizers, etc. may be used at the time of the above-mentioned polymerization reaction.

Furthermore, the thiocarboxylate compound of the present invention has a single polymeric group in the molecule, thus, a pre-polymerization reaction can be carried out to produce a prepolymer and molding can subsequently be done, or the polymerization reaction can be carried out to form pellets and molding can be done subsequently to produce the desired

optical material.

For production of the above-mentioned prepolymer or pellet, standard polymerization reaction methods can be used. In other words, solid polymerization process, solution polymerization process, emulsion polymerization process, suspension polymerization process, sedimentation polymerization process, etc. can be used.

Furthermore, the processes below also can be carried out for the resin with a high refractive index produced by the above-mentioned methods. Namely, dyeing by dispersing with dyes, etc., hardcoating with a hardcoat agent mainly comprising a sol such as a silane coupling and oxides such as silicon, zirconium, antimony and aluminum, and hardcoat agents mainly comprising organic polymers, antireflecting treatments consisting of depositing a thin film of a metal oxide such as SiO_2 , TiO_2 or ZrO or coating of a thin film of an organic polymer, antistatic treatment, etc. can be carried out.

[Effect of the invention]

The polymer produced by performing the polymerization reaction for the thiocarboxylate compound of the present invention has a high refractive index, and excellent transparency, weather resistance, and impact resistance also are achieved. Therefore, the resin with a high refractive index made of a homopolymer of the thiocarboxylate compound of the present invention or a copolymer of the above-mentioned compound and a copolymerizable monomer can be used effectively as an organic glass, for example, for optical lenses for eyeglasses, lenses for optical instruments, as well as for prisms, as a substrate for optical disks, for optical fibers, etc.

[Application Examples]

In the following, the present invention is explained in further detail with specific application examples, but the present invention is not limited to these application examples.

In this case, the identification of the thiocarboxylate compound produced in the present invention was done using the methods described below.

(1) IR spectral analysis

The sample was placed between KBr boards and the measurement was made with the material in the form of a thin film using the IR-440, product of Shimazu Co., Ltd.

(2) $^1\text{H-NMR}$ spectral analysis

The sample was diluted with CDCl_3 , and a measurement was performed with the tetramethyl silane as the internal standard using PMX-60S1 (60 MHz), product of Nihon Denshi Co., Ltd.

(3) Elemental analysis

An analysis was carried out for carbon and hydrogen with the CHN-corder, Model MT-2, product of Yanagimoto Co., Ltd., and a measurement was made for sulfur using the flask burning method.

(4) Refractive index ($n\text{D}^{20}$)

Measurement was performed for the refractive index at a temperature of 20EC by an Abbe refractometer (Model 3T) product of Atago (Ltd.).

Furthermore, a measurement was performed for the properties of the resin with a high refractive index produced in application examples according to the test methods described below.

(1) Refractive index ($n\text{D}^{20}$), Abbe number ($\nu //\text{Nu} //$)

Measurements were made for the refractive index and Abbe number at a temperature of 20EC by an Abbe refractometer (Model 3T) product of Atago (Ltd.). For the contact solution, bromonaphthalene was used.

(2) Surface appearance

A visual evaluation was performed.

[p. 8]

(3) Weather resistance

A sample was position in Long-life Xenon Fadometer, (Model FAC-25AX-HC) product of Suga Testing Machines (Ltd.), an exposure was provided to xenon rays for 100 hours, and the degree of discoloring of the sample was examined visually and those having a degree of discoloring less than that of polystyrene are indicated by //circle//, and those having a degree of discoloring slightly higher than or about the same as polystyrene are indicated by ∈//triangle// and those having a higher degree of discoloring are indicated by x.

(4) Impact resistance

A steel ball with a specific weight was dropped onto a sample sheet punched out to form a disc with a thickness of 2 mm and a diameter of 65 mm from a height of 127 cm, and the maximum weight from which the steel ball was dropped that did not cause breakage in the sample disc was measured. Subsequently, a classification was made according to grades A~E in the following Table I.

Table I

| Weight of steel ball | Grade |
|-----------------------------------|-------|
| 80 g or higher | A |
| 80 g or less but higher than 60 g | B |
| 60 g or less but higher than 40 g | C |
| 40 g or less but higher than 20 g | D |
| 20 g or less | E |

In this case, copolymerizable monomers used in the following application examples are represented by the codes explained below. Furthermore, the number in [] is the refractive index of the homopolymer.

St: Styrene [1.590]

ClSt: Chlorostyrene (mixture of o-member and m-member) [1.610]

DVB: Divinyl benzene [1.615]

BzMA: Benzyl methacrylate [1.568]

ClBzMA: Monochloro benzyl methacrylate [1.582]

BMEPP: 2,2-bis(4-methacryloyloxy ethoxy phenyl) propane [1.558]

Br₄ABMEPP: 2,2-bis(4-methacryloyloxy ethoxy-3,5-dibromophenyl) propane [1.604]

DATP: Diallylterephthalate [1.572]

Furthermore,  is a vinyl group and

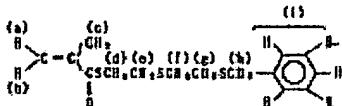
 an isopropenyl group.

Application Example 1

24.4 g (0.10 mole) of di(2-mercaptoproethyl)sulfide monobenzyl thioether, 11.1 g (0.11 mole) of triethylamine and 100 ml of anhydrous chloroform were charged to a three-neck flask equipped with a thermometer, stirring device, and dropping funnel and cooling was performed to 0EC. Subsequently, 12.6 g (0.12 mole) of methacrylic acid chloride was slowly added dropwise as while stirring was provided. At this time, the reaction temperature was maintained at 0~5EC, and further stirring was performed for 1 hour at a temperature of 20EC after the above-mentioned addition was completed. Then, the reaction mixture was poured into water, washing of the organic layer was done with a dilute sodium carbonate solution and a water wash was provided. Drying of the organic layer was then done with anhydrous magnesium chloride and further solvent removal was carried out under vacuum. A purification treatment was performed for the oily substance produced using column chromatography (filler: silica gel, developer: chloroform) and as a result, 18.5 g of the target benzyl thiomethacrylate thioethyl thioethyl was produced in the form of a colorless, transparent, viscous material. The refractive index of the material produced was 1.605. The IR chart for the material produced is shown in Fig. 1. As shown in the figure, the intense absorption of the carbonyl group is observed at 1670 cm⁻¹, and absorption based on an end double bond is observed at 1640 cm⁻¹.

Furthermore, ¹H-NMR (based on tetramethylsilane in CDCl₃ solvent, ppm) chart is shown in Fig. 2. As a result, three peaks based on the hydrogen of methyl group (c) were observed at δ 1.93 as a doublet of coupling constant 2 Hz, eight peaks based on the hydrogens of methylene (d), (e), (f) and (g) were observed at δ 2.4~3.3 as a multiplet, two peaks based on the hydrogen of benzyl position (h) were observed at δ 3.7 as a singlet, a peak based on the

hydrogen of vinyl group (a) was observed at around δ 5.6 as a multiplet, a peak based on the hydrogen of the vinyl group (b) was observed at around δ 6.1 as a multiplet, five peaks based on the hydrogen of phenyl group (i) were observed at around δ 7.1 as a multiplet,



respectively.

[p. 9]

In this case, values obtained by elemental analysis were C: 57.62% (57.65%), H: 6.40% (6.45%), S: 30.82% (30.78%) (the theoretical values are shown in ()) and correspond well with the calculated values.

Application Example 2

2.30 g (0.10 mole) of di(2-mercaptoproethyl)sulfide monobenzyl thioether, 11.1 g (0.11 mole) of triethylamine and 100 ml of anhydrous chloroform were charged to a three-neck flask equipped with a thermometer, stirring device, and dropping funnel and cooling was performed to 0EC. Subsequently, 12.6 g (0.12 mole) of methacrylic acid chloride was slowly added dropwise as stirring was being performed. At this time, the reaction temperature was maintained at 0~5EC, and stirring was performed for 1 hour at a temperature of 20EC after the above-mentioned addition was completed. Then, the reaction mixture was poured into water, washing of the organic layer was done with a dilute sodium carbonate solution and a water wash was further performed. Drying of the organic layer was done with anhydrous magnesium chloride and further removal of the solvent was carried out under vacuum. A

purification treatment was performed for the oily substance produced using column chromatography (filler: silica gel, developer: chloroform) and as a result, 16.7 g of the target phenylthiomethacrylate thioethyl thioethyl was produced in the form of a colorless, transparent, viscous material. The refractive index of the material produced above was 1.609.

Furthermore, values obtained by elemental analysis were C: 56.29% (56.33%), H: 6.04% (6.08%), S: 32.29% (32.23%) (the theoretical values are shown in ()) and correspond well with the calculated values.

Application Example 3

24.4 g (0.1 mole) of di(2-mercaptop ethyl) sulfide monobenzyl ether, 8.7 g (0.11 mole) of pyridine and 200 ml of anhydrous benzene were charged to a three-neck flask equipped with a thermometer, stirring device, and dropping funnel and cooling was performed to 0EC. Subsequently, 10.0 g (0.11 mole) of methacrylic acid chloride was slowly added dropwise as stirring was performed. At this time, the reaction temperature was maintained at 0~5EC, and further stirring was provided for 1 hour at a temperature of 20EC after the above-mentioned addition was completed. Then, the reaction mixture was poured into water, washing of the organic layer was done with a dilute sodium carbonate solution and a water wash was provided. Drying of the organic layer was done with anhydrous magnesium chloride and further removal of the solvent was carried out under vacuum. A purification treatment was performed for the oily substance produced using column chromatography (filler: silica gel, developer: chloroform), and as a result, 15.4 g of the target benzyl thiomethacrylate thioethyl thioethyl was produced in the form of a colorless, transparent, viscous material. The

refractive index of the material produced above was 1.610. Furthermore, values obtained by elemental analysis were C: 56.39% (56.33%), H: 6.02% (6.08%), S: 32.20% (32.23%) (the theoretical values are shown in ()) and correspond well with the calculated values.

Application Examples 4~17

Production of thiocarboxylate compounds was carried out as in the case of Application Example 1 with the raw materials shown in Table II below. Properties of the thiocarboxylate compounds produced are shown in Table II as well.

Table II

| Application Example | Thiocarboxylate compound | Characteristics | Refractive Index nD^{20} | ν/cm^{-1} (C=O) | Elemental analysis, theoretical values shown in () | | |
|---------------------|--------------------------|--|----------------------------|----------------------------|---|----------------|------------------|
| | | | | | C | H | S |
| 4 | | Colorless, transparent, viscous material | 1.614 | 1665 | 54.86 (54.89) | 5.63 (5.67) | 33.89 (33.82) |
| 5 | | " | 1.597 | 1670 | 59.91 (59.95) | 7.11 (7.10) | 28.28 (28.25) |
| 6 | | " | 1.600 | " | 58.86 (58.85) | 6.77 (6.79) | 29.53 (29.46) |
| 7 | | " | 1.593 | " | 60.92 (60.97) | 7.38 (7.39) | 27.19 (27.13) |
| 8 | | " | 1.613 | " | 55.56 (55.59) | 6.16 (6.18) | 35.82 (35.77) |
| 9 | | " | 1.610 | " | 54.76 (54.79) | 6.44 (6.49) | 34.48 (34.42) |
| 10 | | " | 1.613 | " | 52.73 (52.73) | 6.50 (6.52) | 37.09 (37.05) |
| 11 | | " | 1.611 | " | 50.53 (50.51) | 5.09 (5.15) | 28.96 (28.89) |

Table II (cont.)

| | Thiocarboxylate compound | Characteristics | Refractive Index nD^{20} | IR (cm^{-1}) $\nu / \text{null} / (\text{C}=\text{O})$ | Elemental analysis, theoretical values shown in () | | |
|------------------------|--------------------------|--|----------------------------|--|---|----------------|------------------|
| | | | | | C | H | S |
| Application Example 12 | | Colorless, transparent, viscous material | 1.622 | 1670 | 38.30 (38.31) | 3.80 (3.86) | 20.52 (20.45) |
| Application Example 13 | | " | 1.614 | " | 53.51 (53.59) | 6.17 (6.18) | 35.85 (35.77) |
| Application Example 14 | | " | 1.612 | " | 64.87 (64.90) | 6.21 (6.22) | 24.80 (24.75) |
| Application Example 15 | | " | 1.585 | " | 43.26 (43.21) | 6.58 (6.36) | 42.98 (43.26) |
| Application Example 16 | | " | 1.579 | " | 45.70 (45.72) | 6.58 (6.82) | 40.77 (40.69) |
| Application Example 17 | | " | 1.587 | " | 44.38 (44.55) | 7.03 (6.80) | 42.96 (43.25) |

[p. 11, lower part amended p. 16]

Application Example 18

As a radical polymerization initiator, 1 part by weight of t-butyperoxy-2-ethylhexanate was added to 100 parts by weight of the thiocarbonate compounds produced in the above-mentioned Application Examples 1~17 and thorough mixing was performed. The above-mentioned mixed solution was poured into a die made of a gasket comprising a glass sheet and ethylene-vinyl acetate copolymer and a polymerization reaction was performed. In this case, the above-mentioned polymerization reaction was carried out in an air furnace and the temperature was slowly increased from 30EC to 90EC in 18 hours and the temperature was then retained at 90EC for 2 hours. After the above-mentioned polymerization reaction, the die was removed from the air furnace, natural cooling was performed, and the polymer was removed from the glass die. Measurement was performed for the properties of the polymers produced and the results obtained are shown in Table III.

Table III

| No. | Application Example No. of thiocarboxylate compound | Surface appearance | Refractive index nD | Abbe number (ν) | Weather resistance | Impact resistance |
|-----|---|------------------------|---------------------|-----------------|--------------------|-------------------|
| 1 | 1 | Colorless, transparent | 1.650 | 33 | //circle// | A |
| 2 | 2 | " | 1.656 | 30 | //circle// | A |
| 3 | 3 | " | 1.660 | 32 | //circle// | A |
| 4 | 4 | " | 1.665 | 29 | //circle// | A |
| 5 | 5 | " | 1.635 | 34 | //circle// | A |
| 6 | 6 | " | 1.641 | 31 | //circle// | A |
| 7 | 7 | " | 1.626 | 32 | //circle// | A |
| 8 | 8 | " | 1.665 | 29 | //circle// | A |
| 9 | 9 | " | 1.660 | 32 | //circle// | A |
| 10 | 10 | " | 1.668 | 31 | //circle// | A |
| 11 | 11 | " | 1.662 | 29 | //circle// | A |
| 12 | 12 | " | 1.663 | 32 | //circle// | A |
| 13 | 13 | " | 1.665 | 32 | //circle// | A |
| 14 | 14 | " | 1.664 | 31 | //circle// | A |
| 15 | 15 | " | 1.639 | 34 | //circle// | A |
| 16 | 16 | " | 1.617 | 35 | //circle// | A |
| 17 | 17 | " | 1.639 | 34 | //circle// | A |

Application Examples 19~22

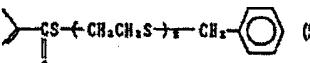
For 100 parts by weight of styrene, benzyl thiomethacrylate thioethyl thioethyl was added at the weight ratio shown in Table IV, 1 part by weight of t-butylperoxy-2-ethyl hexanate was added as a radical polymerization initiator and thorough mixing was performed. In this case, an air furnace was used and the temperature was slowly increased from 30EC to 90EC in 18 hours and the temperature was then retained at 90EC for 2 hours. After the above-mentioned polymerization reaction, the removal of the die was performed from the air furnace,

natural cooling was provided, and the polymer was removed from the glass die. Measurement was performed for the properties of polymers produced and the results obtained are shown in Table IV.

Comparative Example 1

In Application Examples 19~22 above, the benzyl thiomethacrylate thioethyl thioethyl was omitted and processing was done as in Application Examples 19~22. And the results obtained are shown in Table IV.

Table IV

| | Copolymerizable monomer | Thiocarbonate compound (parts by weight) | Refractive Index nD ²⁰ | Impact resistance |
|------------------------|-------------------------|---|-----------------------------------|-------------------|
| Application Example 19 | St |  | 1.593 | C |
| " 20 | " | " (00) | 1.595 | C |
| " 20 | " | " (05) | 1.598 | B |
| " 20 | " | " (20) | 1.600 | B |
| Comparative Example 1 | " | " (0) | 1.590 | E |

[p. 12, Amended p. 17]

Application Examples 23~30

Mixed solutions comprising copolymeric monomers having an aromatic ring and benzyl thiomethacrylate thioethyl thioethyl shown in the following Table V were used and a treatment was performed as in the case of Application Examples 19~22. Measurement was performed for properties of the polymers produced and the results obtained are shown in Table V.

Comparative Examples 2~9

In Application Examples 23~30, benzyl thiomethacrylate thioethyl thioethyl was omitted and a treatment was performed as in the case of Application Examples 23~30. And the

results obtained are shown in Table V.

Table V

| | Copolymerizable monomers (parts by weight) | Thiocarbonate compounds (parts by weight) | Refractive index nD ²⁰ | Impact resistance |
|------------------------|--|---|-----------------------------------|-------------------|
| Application Example 23 | CISt (100) | | 1.615 (15) | B |
| Comparative Example 2 | " (100) | " (0) | 1.610 | E |
| Application Example 24 | DVB (100) | " (20) | 1.621 | B |
| Comparative Example 3 | " (100) | " (0) | 1.615 | E |
| Application Example 25 | BzMA (100) | " (10) | 1.575 | B |
| Comparative Example 4 | " (100) | " (0) | 1.568 | D |
| Application Example 26 | CIBzMA (100) | " (5) | 1.585 | B |
| Comparative Example 5 | " (100) | " (0) | 1.582 | D |
| Application Example 27 | DATP (100) | " (5) | 1.576 | C |
| Comparative Example 6 | " (100) | " (0) | 1.572 | E |
| Application Example 28 | DVB (60), BzMA (40), | " (15) | 1.603 | B |
| Comparative Example 7 | " (60), " (40) | " (0) | 1.598 | E |
| Application Example 29 | BMEPP (30), CISt (70) | " (10) | 1.599 | B |
| Comparative Example 8 | " (30), " (70) | " (0) | 1.594 | D |
| Application Example 30 | Br4 ABMEPP (30), St (70) | " (15) | 1.601 | A |
| Comparative Example 9 | " (30), " (70) | " (0) | 1.594 | D |

[p. 13, Amended p. 18]

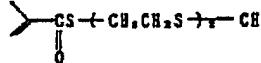
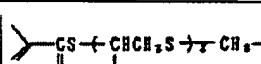
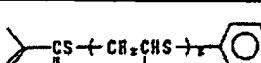
Application Examples 31~43 and Comparative Examples 10~17

Compositions comprising copolymeric monomers having an aromatic ring and thiocarbonate compounds shown in the following Table VI were used and processing was carried out as in the case of Application Examples 19~22. The properties of the polymers produced were measured and the results obtained are shown in Table VI.

Furthermore, thiocarbonate compounds were omitted and a treatment was performed as described above and the results obtained are shown in Table VI as well. Furthermore, the compound shown in the general formula below was used as a thiocarbonate compound and a treatment was performed as described above, and the results obtained are also shown in Table VI as [Comparative Example 17].

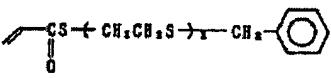
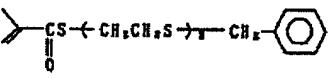
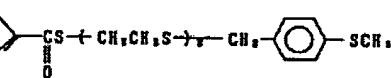
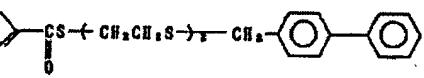


Table VI

| | Copolymerizable monomers (parts by weight) | Thiocarbonate compounds (parts by weight) | | Refractive index nD^{20} | Impact resistance |
|------------------------|---|---|------|-------------------------------|-------------------|
| Application Example 31 | DVB (70), BzMA (30) |  | (10) | 1.602 | C |
| " 32 | " (70), " (30) |  | (5) | 1.603 | C |
| Comparative Example 10 | " (70), " (30) | XXX | | 1.601 | E |
| Application Example 33 | DVB (60), ClBzMA (40) |  | (20) | 1.612 | B |
| Comparative Example 11 | " (60), (40) | XXX | | 1.602 | E |
| Application Example 34 | St (50), DVB (50) |  | (10) | 1.605 | C |
| " 35 | " (50), " (50) |  | (10) | 1.606 | C |
| " 36 | " (50), " (50) |  | (5) | 1.606 | C |
| " 37 | " (50), " (50) |  | (10) | 1.608 | C |
| Comparative Example 12 | " (50), " (50) | XXX | | 1.603 | E |

[p. 14, Amended p. 19]

Table VI (cont.)

| | Copolymerizable monomers (parts by weight) | Thiocarbonate compounds (parts by weight) | | Refractive index nD^{20} | Impact resistance |
|------------------------|--|--|------|----------------------------|-------------------|
| Application Example 38 | St (60), BMEPP (40) |  | (10) | 1.582 | B |
| Comparative Example 13 | " (60), " (40) | XXX | | 1.577 | D |
| Application Example 39 | ClSt (70), Br4 ABMEPP (30) |  | (15) | 1.615 | A |
| " 40 | " (70), " (30) |  | (10) | 1.613 | A |
| Comparative Example 14 | " (70), " (30) | XXX | | 1.608 | D |
| Application Example 41 | ClSt (50), BMEPP (50) |  | (10) | 1.617 | C |
| Comparative Example 15 | " (50), " (50) | XXX | | 1.613 | E |
| Application Example 42 | BzMA (70), BMEPP (30) |  | (10) | 1.574 | C |
| " 43 | " , " |  | (10) | 1.574 | C |
| Comparative Example 16 | " , " | XXX | | 1.565 | E |
| Comparative Example 17 | " , " |  | (10) | 1.568 | D |

4. Brief description of figures

Fig. 1 and Fig. 2 are infrared absorption spectra and ^1H -nuclear magnetic resonance spectra graphs, respectively, for the thiocarboxylate compound produced in Application Example 1,

Applicant: Tokuyama Soda Corp.

[p. 15]

Fig. 1

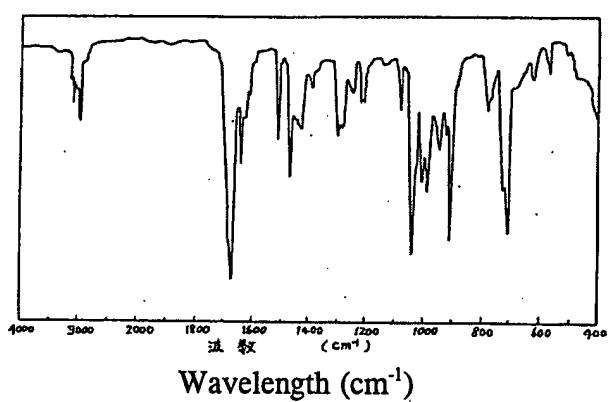


Fig. 2

